POST-COMBUSTION AND PRE-COMBUSTION CO_2 CAPTURE SOLID SORBENTS

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Introduction

Fossil fuels supply more than 98 percent of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas, carbon dioxide. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of greenhouse gases. Commercial CO_2 capture technology that exists today is expensive and energy intensive. Improved technologies for CO_2 capture are necessary to achieve low energy penalties. Pressure swing adsorption/sorption (PSA/PSS) and temperature swing adsorption/sorption (TSA/TSS) are some of the potential techniques that could be applicable for removal of CO_2 from both high- and low-pressure gas streams.

NETL research group has developed a novel solid sorbent utilizing a liquid-impregnation technique. The sorbent is capable of capturing CO_2 in the presence of steam at ambient temperatures and can be regenerated at temperatures below 80 °C. Recent systems analysis conducted at NETL indicate that this process is economically favorable. The liquid-impregnated solid sorbent showed higher capacities during both low and high pressure tests.

According to a 1999 IEA report, the PSA and TSA processes may be more suitable for CO_2 capture from gasification processes. The system analysis conducted in the Netherlands shows that the PSA and TSA systems would be even more energy efficient for integrated gasification combined cycle (IGCC) systems if the sorbents were operational at warm gas temperatures (250–350 °C).[1] To address this problem, researchers at NETL developed a novel magnesium-based sorbent that can capture CO_2 at 200–315 °C and are regenerable at 375 °C. The capture process with this novel warm gas CO_2 removal sorbents involves a chemical reaction. The sorbent has a high CO_2 sorption capacity at 200-400 °C, which is considerably higher than that of the Selexol process.

NETL researchers have developed a novel sodium-based sorbent at that can capture CO_2 at 600 °C. The sorbent is regenerable at 900 °C and 1 atm. This sorbent may be suitable for more severe capture conditions as well as sorbent-enhanced water gas shift reaction.

The objective of this work is to develop regenerable sorbents that have high selectivity, efficient regenerability, and high adsorption capacity for CO_2 over wide temperature ranges. These properties are critical for the success of the PSA/PSS and TSA/TSS processes.

Experimental

The liquid-impregnated solid sorbent pellets suitable for fixed bed applications were prepared at Süd-Chemie utilizing the procedure provided by NETL.[2] Competitive gas adsorption studies were conducted in a bench-scale fixed-bed reactor (2 in. diameter with 6 in. bed height) at 1 atm ($\sim 1.01 \times 10^5$ Pa) and at 30 °C using a gas mixture with a composition that represented flue gas (15 percent CO_2, 82 percent nitrogen, and 3 percent oxygen saturated with water vapor) . The

[1] I. Smith, "CO_2 Reduction Prospects for Coal," IEA research report, ISBN 92-9029-336-5, 1999.
[2] R.V. Siriwardane, "Solid Sorbents for Removal of Carbon Dioxide from Gas Streams at Low Temperatures," U.S. Patent 6,908,497 B1, June 21, 2005.

regeneration was conducted at 80 °C with steam and N_2 mixture. A liquid impregnated solid sorbent (<700 microns) suitable for other reactor bed applications such as fluidized reactor bed was also prepared. These sorbents were also tested in a lab scale reactor with simulated flue gas at 30-60°C and were regenerated at 80 °C.

Testing was conducted with the magnesium-based solid sorbent at 200–250 °C in flow reactors at 10-30 atm and was regenerated at 375 °C at both 1 atm and 10.2 atm with steam and N_2. The space velocity used for the test was 250-1000 h^{-1}.

Testing was conducted with the sodium-based solid sorbent at 600°C in a flow reactor at 1 atm. Regeneration was performed at 885°C at 1 atm with steam and N_2. The gas hourly space velocity for both capture and regeneration was 500 h^{-1}. The sorbent was also employed during water gas shift reaction testing to evaluate its ability to enhance the reaction. Sorbent-enhanced water gas shift testing was performed at 300-600°C at 1-20 atm with a reactor feed consisting of 15 percent CO, 18 percent H_2O, and 67 percent He.

Results and Discussion

Atmospheric Pressure Tests with the Liquid-Impregnated Solid Sorbent

When the sorbent was tested at an atmospheric pressure of 30 °C, it was able to remove CO_2 from 15–17 percent to parts per million (ppm) levels from a gas mixture containing 15–17 percent CO_2, 3 percent O_2, and 82 percent N_2 saturated with water. The removal efficiency was 99 percent at 1,000 hr-1 space velocity. Multi-cycle tests conducted with the fixed bed sorbent showed that the sorbent reactivity was stable indicating that the regeneration of the sorbent at 80 °C with steam did not affect the sorbent's performance. The sorbent CO_2 sorption capacity was 1.5–2.0 moles per kg. Preliminary systems analysis conducted at NETL indicated that the CO_2 removal utilizing the solid sorbent is more economical than the process with liquid amines since the regeneration of the solid sorbent requires less energy.[3] Since steam does not affect the sorbent's performance, regeneration in the presence of steam would be a reasonable choice. The ability to regenerate the sorbent at a lower temperature and the resistance to steam are advantages of this novel, ambient-temperature CO_2 removal sorbent. The sorbent (< 600 microns) prepared for other reactor bed showed 99% removal efficiency and CO_2 capacity of about 1.5 moles per kg at 40 °C. This is very close to the acceptable CO_2 capture capacities identified by the reactor design studies.

Atmospheric Pressure Tests with the Liquid-Impregnated Solid Sorbent Suitable for Fluidized-Bed and Isothermal-Bed Reactors

The sorbent was prepared with a particle size less than 600 μm as required for fluidized-bed and isothermal-bed reactors. The reactor design studies conducted at NETL indicated that heat of regeneration of the sorbent is strongly depended on the specific heat capacity of the sorbent, the CO_2 capture delta capacity (difference between CO_2 sorption capacity at the absorption temperature and the CO_2 sorption capacity at regeneration temperature) and the heat of sorption of CO_2. For the liquid impregnated clay sorbent, the required minimum CO_2 delta capacity is estimated to be about 1.6-1.9 mol/kg for isothermal-bed reactors. However, this requirement may be lower for the fluidized-bed reactors. The sorbent (<600 μm) was tested with simulated flue gas; results of the testing yielded a 99 percent removal efficiency of CO_2 and a capture capacity of approximately 2.1 mol CO_2/kg of sorbent at 40 °C as shown in Figure 1. Since the particle density of the sorbent is ~2 g/cm3, the corresponding CO_2 capture capacity (volume basis) is approximately 4.6 mol/liter of sorbent. The sorbent can be regenerated at 80-100 °C; since steam will likely be utilized during regeneration, the

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[3] T. Tarka, "System Analysis of NETL Solid Sorbent," internal report, U.S. Department of Energy, NETL, 2005.

majority of the regenerations were conducted at 100 °C. The CO_2 capture delta capacity for sorption at 40 °C and regeneration at 100 °C was determined to be 1.6 mol/kg (3.2 mol/liter) and 1.3 mol/kg (2.6 mol/liter) for sorption at 60 °C. The value obtained at 40 °C is very close to the acceptable CO_2 capture delta capacities identified by the reactor design studies. A 10-cycle test performed with capture at 60 °C and regeneration at 100 °C showed stable reactivity. The sorbent preparations were also made in collaboration with Süd Chemie, Inc. to develop materials with more attrition resistance.

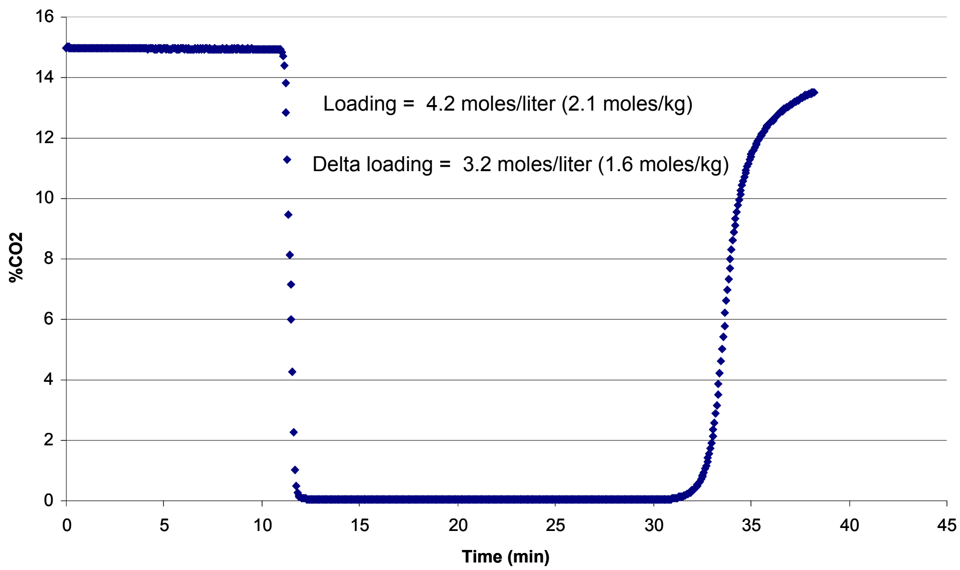

FIGURE 1. Lab-scale flow reactor test data with sorbent (particle diameter < 600 μm) suitable for fluidized-bed/isothermal-bed reactors at 1 atm; 40 °C; GHSV ~ 500 h^{-1}; Feed composition = 16% CO_2, 3% O_2, 82% N_2, saturated with water vapor.

Warm Temperature Sorbent

The CO_2 capture sorbents that operate at 200–315 °C would be very useful for IGCC applications. The water gas shift reactor converts the gas to CO_2 and H_2 at 200–350 °C. A pure hot H_2 stream can be obtained if CO_2 is removed at 200–315 °C. Magnesium-based sorbents prepared at NETL were tested in a lab-scale reactor at 200–250 °C at 10.2 atm with 28 percent CO_2 in He saturated with steam. Regeneration was conducted at 375 °C and 10.2 atm. A 10-cycle flow reactor test conducted at 250 h^{-1} space velocity with about 3 grams of magnesium-based sorbent indicated that the sorbent has a very high CO_2 capture capacity (approx. 4 moles per kg) as shown in Table 1.

Further testing was conducted at a bench scale to evaluate process variables (i.e., temperature, pressure, H_2O feed content, etc.). Testing was conducted at 200-250 °C, 10-30 atm, with H_2O content between 10-30 percent and with 10 percent CO_2. Testing revealed that an increase in pressure and/or H_2O concentration resulted in improved CO_2 capture capacity. The test data at 10.2 atm and 15 percent H_2O is shown in Figure 2.

Regenerable sorbents at 200–315 °C with high CO_2 capture capacities are not reported in the literature, and these novel sorbents offer great promise for IGCC applications. The high capacities will contribute to low regeneration cost and small vessel size. The regeneration temperature of the sorbent is 375 °C, and the temperature swing from absorption to regeneration is very low. Preliminary system analysis conducted at NETL showed promising data with restricted use of steam during regeneration.

Table 1. Test conditions and capture capacities during the 10-cycle test of the magnesium-based warm gas temperature CO_2 removal sorbent.

	CO_2 Sorption			Regeneration	
Cycle	T (°C)	P (atm)	Capacity (mol/kg)	T (°C)	P (atm)
1	200	6.8	1.47	375	1.0
2	250	6.8	2.11	375	1.0
3	250	10.2	2.13	375	1.0
4	200	10.2	2.84	375	1.0
5	200	6.8	2.40	375	1.0
6	200	10.2	3.46	375	10.2
7	200	10.2	4.09	375	10.2
8	200	10.2	4.14	375	10.2
9	200	10.2	4.27	375	10.2
10	200	10.2	3.22	-------	-------

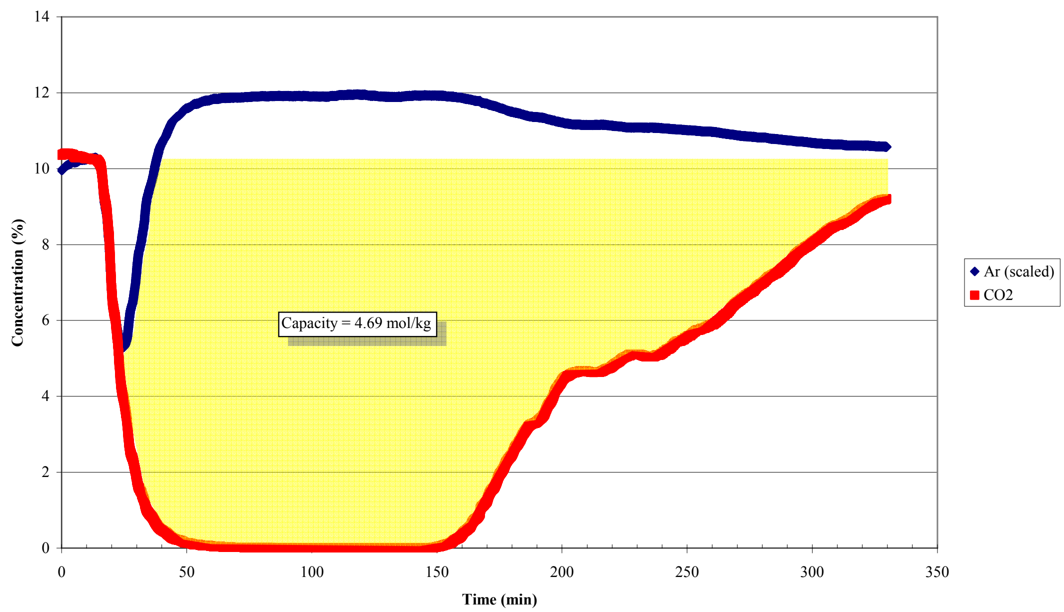

Figure 2. Bench-scale testing with magnesium-based sorbent. Test performed at 200°C, 10.2 atm, 250 h^{-1}. Feed composition = 10% CO_2, 15% H_2O, 10% Ar, bal. N_2.

High Temperature Sorbent

Sorbents that operate at temperatures higher than 300 °C would be useful for more severe capture requirements. Sodium-based sorbents prepared at NETL were tested in a bench-scale reactor at 600 °C and 1 atm with a feed composition of 10 percent CO_2, 30 percent H_2, 15 percent H_2O, and 45 percent He at a space velocity of 500 h^{-1}. Regeneration was performed at 885 °C and 1 atm in flowing steam and He. CO_2 capture capacity of this sorbent was determined to be very high (5-7 moles per kg). A multi-cycle test was conducted; capture capacity of the final capture cycle was greater than the first capture cycle. This sorbent also enhanced the water gas shift reaction and converted CO/H_2O to H_2 without an additional catalyst as shown in Figure 3.

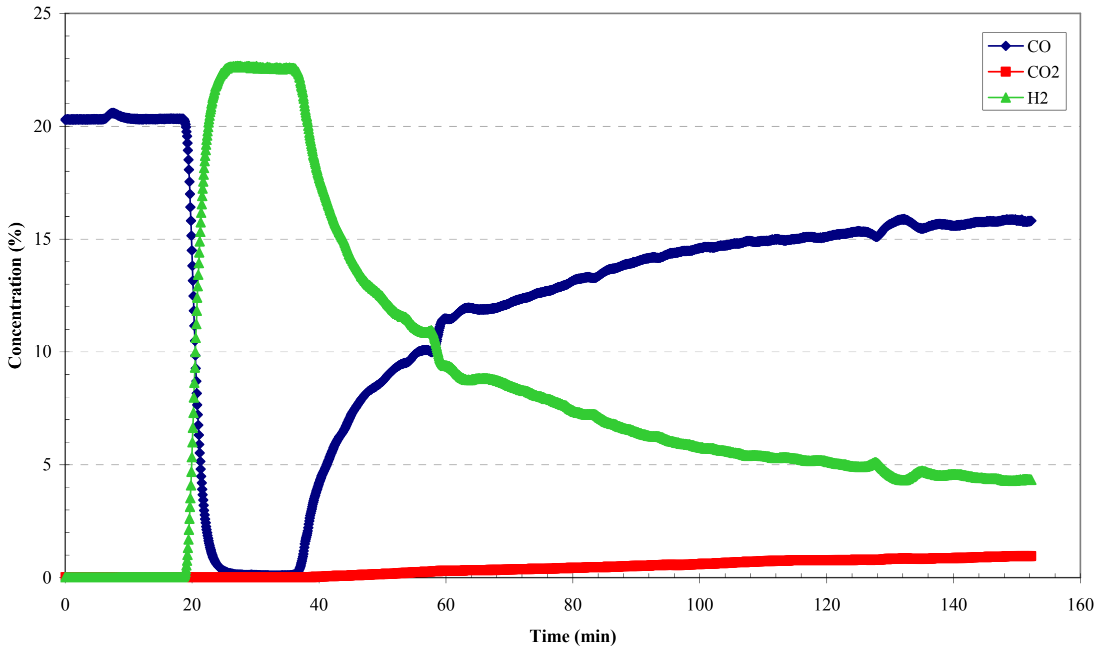

Figure 3. Bench-scale sorbent-enhanced water gas shift reaction testing with sodium-based sorbent. Test performed at 600°C, 1 atm, 500 h^{-1}. Feed composition = 15% CO, 18% H_2O, 67% He.

Summary

The novel liquid-impregnated solid sorbent showed stable CO_2 sorption performance at ambient temperature and atmospheric pressure during a multi-cycle test and regenerability below 80 °C. The sorbent's performance was not affected due to the presence of steam. The capture capacity of the liquid-impregnated solid sorbent is significantly higher at 20 atm. Acceptable sorbent capacity and delta loading was achieved for 40 °C sorption and 100 °C regeneration.

The novel magnesium-based sorbent was able to capture CO_2 (4 moles per kg) at 200–250 °C and 10.2 atm, and it was possible to regenerate the sorbent at 375 °C and 10.2 atm. The performance was stable during a 10-cycle test.

The novel sodium-based sorbent was able to capture CO_2 (5-7 moles per kg) at 600 °C and 1 atm; it was possible to regenerate the sorbent at 885°C and 1 atm. The performance was stable over a multi-cycle test. This sorbent was also able to enhance the WGS reaction to produce H_2 without a catalyst.

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